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Evolving Concepts of Subsurface Contaminant Transport

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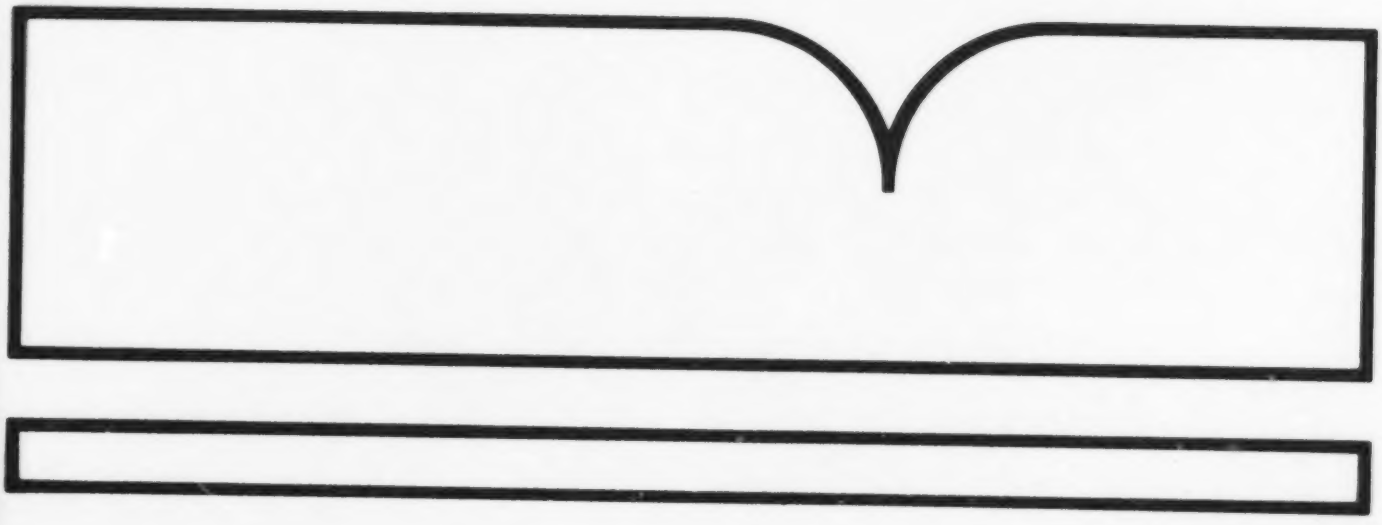

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16. ABSTRACT

Currently, a large gap exists between theoretical advances in the understanding of how various natural processes affect subsurface contaminant transport, and our ability to translate those advances into practical applications. The lack of truly representative and reliable field tests for important parameters that are used to characterize these natural processes is a major stumbling block, as is the reluctance to use state-of-the-art tools and information in conventional site investigations. Incorporation of state-of-the-art techniques in site characterization efforts should be encouraged, however, as total costs of investigating and remediating a site would be lowered due to the improved remedial action designs that would result. Moreover, the feedback afforded by incorporating state-of-the-art techniques in site characterization efforts would considerably strengthen and advance efforts to elucidate the mechanisms controlling subsurface contaminant transport.

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FEATURE

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Evolving concepts of subsurface contaminant transport

Joseph F. Keely, Marvin D. Piwoni, John T. Wilson

For nearly two decades, environmental contamination from domestic, industrial, and agricultural activities has become the focus of increasing concern. This environmental awareness was stimulated, in part, by an explosive growth in the development of data collection and interpretation methods. Unprecedented advances in chemical analysis became commonplace; "parts per million" gave way to "parts per billion" as the most common unit of chemical concentration. Computers were streamlined from the "mainframe" to the "mini" to the "micro," and computer software became so sophisticated that the use of artificial-intelligence packages was possible. Concurrently, identification and removal of sources of environmental contamination became major societal goals.

These trends inspired a heightened appreciation of the need for intensive investigations of the natural processes that control the transport and fate of contaminants in the environment. Initially, these investigations were directed toward alleviating undesirable impacts to the most visible natural resources such as streams, lakes, estuaries, and the atmosphere. By the mid-1970s, however, common perceptions of which parts of the environment were most threatened began to change as the realization took hold that those parts which are out-of-sight should not also be out-of-mind. Consequently, much more attention was given to defining the natural processes that control the fate and transport of contaminants in the subsurface.

Levels of understanding

Much of the attention devoted to natural processes in the subsurface has come in the form of applying concepts derived from work in other environmental media. Theories of organic chemical sorption to stream sediments, for example, have been applied to subsurface contaminant transport problems without modification. Only recently have substantial advances been made in understanding subsurface sorption processes. As a consequence, state of the art in groundwater contamination studies lags a considerable distance behind the "state of the science." What is actually put into routine use differs from accepted theory because of simplifications, difficulties in measuring certain coefficients and constants, and so on. This is illustrated, for instance, by the use of linearized sorption constants for contaminants shown to produce nonlinear isotherms. Similarly, state of the science in groundwater contamination studies lags behind the "state of knowledge," or what has been shown to occur despite the lack of theories which can adequately describe or predict it. This is exemplified by data from field investigations which indicate that sorbed contaminants may be transported through the subsurface in association with ultrafine particulates.

It is therefore useful to view subsurface contaminant transport on these three levels of understanding: conceptual (state of the knowledge), theoretical (state of the science), and practical (state of the art). This discussion will focus on changing perceptions of how natural processes control the transport and fate of contaminants in the subsurface. Specifically, emphasis will be placed on the need for fresh conceptualizations of transport mechanisms in the subsurface to overcome limitations imposed by current theoretical assumptions. How simplifications of some natural process theories complicate others in practical applications will also be highlighted. Finally, the usefulness of tentative research results in developing better understandings of cause-and-effect relationships for site-specific problems will be noted.

Overview of subsurface transport

There are many natural processes that affect chemical transport from point to point in the subsurface. These natural processes can be arbitrarily divided into three categories: physical, chemical, and biological (Table 1). Conceptually, contaminant transport in the subsurface is an undivided phenome-

non composed of these processes and their interactions (Figure 1). At this level the transport process may be gestalt; the sum of its parts, measured separately, may not equal the whole because of interactions between the parts. In the theoretical context, a collection of scientific laws and empirically derived relationships comprise the overall transport process. The universally shared premise that underlies theoretical expressions is that there are no interactions, measureable or otherwise.

Significant errors may result from the discrepancy between conceptual and theoretical approaches. Also the simplifications of theoretical expressions used to solve practical problems can cause substantial errors in the most careful analyses. Assumptions and simplifications, however, must often be made in order to obtain mathematically tractable solutions. Because of this, the magnitude of errors that arises from each assumption and simplification must be carefully evaluated. The phrase "magnitude of errors" is emphasized because highly accurate evaluations usually are not possible. Even rough approximations are rarely trivial exercises because they frequently demand estimates of some things which are as yet ill-defined.

Physical processes. Until recently, groundwater scientists studied physical processes to a greater degree than chemical or biological processes. This bias resulted in large measure from the fact that, in the past, groundwater practitioners dealt mostly with questions of adequate water supplies. As quality considerations began to dominate groundwater issues, the need for studies of the chemical and biological factors as well as more detailed representations of physical factors became apparent.

There are two complimentary ways to view the physical processes involved in subsurface contaminant transport: the piezometric (pressure) viewpoint and the hydrodynamic viewpoint. Groundwater problems of yesterday could be addressed by the former, such as solving for the change in pressure head caused by pumping wells. Contamination problems of today also require detailed analyses of wellfield operations, for example, pump-and-treat plume removal; however, solutions depend principally on hydrodynamic evaluations, such as computing groundwater velocity (advection) distributions and dispersion estimates for migrating plumes.

Table 1—Natural processes that affect subsurface contaminant transport.

Physical processes
Advection (porous media velocity)
Hydrodynamic dispersion
Molecular diffusion
Density stratification
Immiscible phase flow
Fractured media flow
Chemical processes
Oxidation-reduction reactions
Radionuclide decay
Ion-exchange
Complexation
Co-solvation
Immiscible phase partitioning
Sorption
Biological processes
Microbial population dynamics
Substrate utilization
Biotransformation
Adaptation
Co-metabolism

Advection and dispersion. Groundwater velocity distributions can be approximated if the variations in hydraulic conductivity, porosity, and the strength and location of recharge and discharge can be estimated. While there are several field and laboratory methods for estimating hydraulic conductivity, these are not directly comparable because different volumes of aquifer material are affected by different tests. Laboratory permeameter tests, for example, obtain measurements from small core samples and thus give point value estimates. These tests are generally reliable for consolidated rock samples, such as sandstone, but can be highly unreliable for unconsolidated samples, such as sands, gravels, and clays. Pumping tests give estimates of hydraulic conductivity that are averages over the entire volume of aquifer subject to the pressure changes induced by pumping. These give repeatable results, but they are often difficult to interpret. Tracer tests are also used to estimate hydraulic conductivity in the field, but are difficult to conduct properly.

Regardless of the estimation technique used, the best that can be expected is order-of-magnitude estimates for hydraulic conductivity at the field scale appropriate for site-specific work. Conversely, porosity estimates that are accurate to better than a factor of two can be obtained. Estimation of the strength of nonpoint sources of recharge to an aquifer, such as infiltrating rainfall and leakage from other aquifers, is another order-of-magnitude effort. Similarly, nonpoint sources of discharge, such as losses to gaining streams, are difficult to quantify. Estimation of the strength of point sources of recharge or discharge (injection or pumping wells) can be highly accurate.

Consequently, it is not possible to generalize the quality of velocity distributions; they may be accurate to within a factor of two for very simple aquifers, but are more often accurate to an order-of-magnitude at best. This situation has changed little over the past 20 years because better field and laboratory methods for characterizing velocity distributions have not been developed. This, however, is not the primary difficulty associated with defining the advective part of contaminant transport in the subsurface. The primary difficulty is that field tests to characterize physical parameters that control velocity distributions are not incorporated into contamination investigations on a routine basis. The causes seem to be: a perception that mathematical models can "back-out" an approximation of the velocity distribution (presumably eliminating the need for field tests); unfamiliarity with such methods by many practitioners; and a percep-

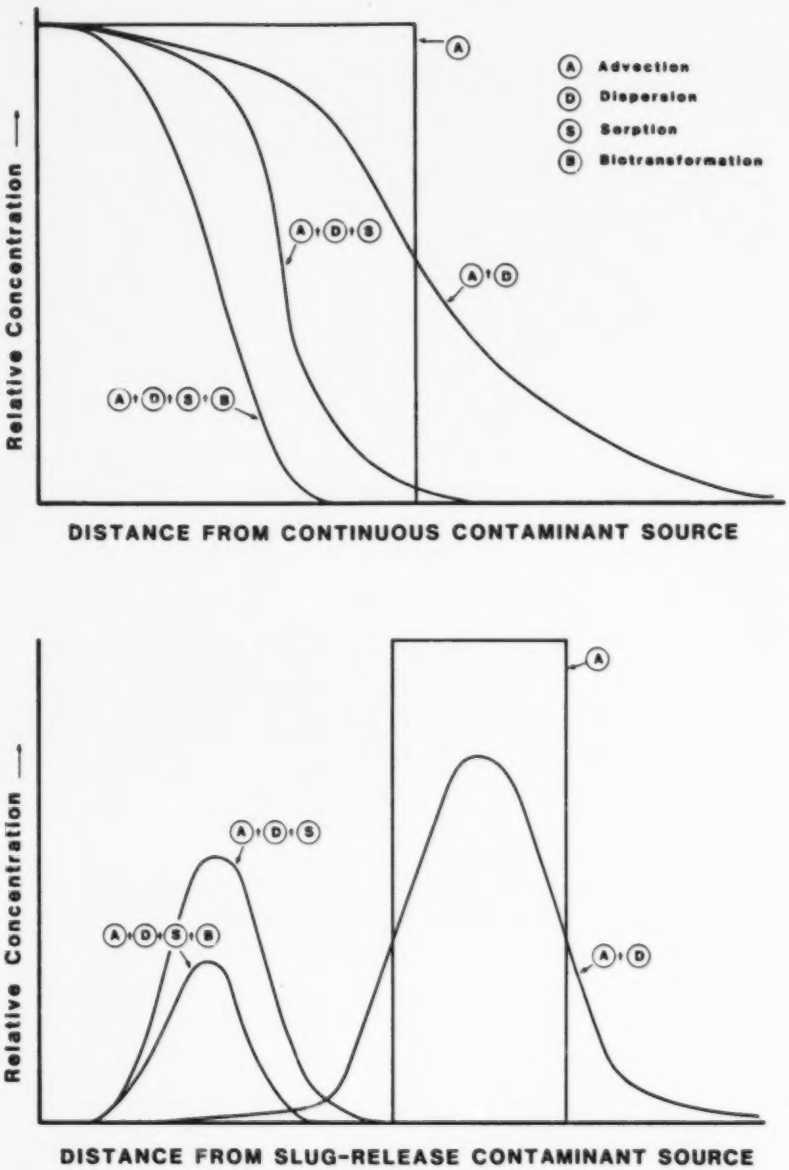

Figure 1—The relative effects of various natural processes on contaminant concentrations as a function of distance from continuous and slug-release sources.

tion that field tests are too expensive. A more field-oriented approach is preferable because the non-uniqueness of modeling results has been amply demonstrated and this leads to uncertain decisions regarding the design of remedies. The conventional approach may be cost-effective with regard to the site investigation phase of a project, but it is not necessarily cost-effective for the remedial action phase or the overall project.

Dispersion estimates are predicated on velocity distribution estimates and their accuracy therefore directly depends on the accuracy of the estimated hydraulic conductivity distribution. Tracer tests have been the primary method used to determine dispersion coefficients until recently. Presently there are suggestions that any field method capable of generating a detailed understanding of the spatial variability of hydraulic conductivity, which in turn could give an accurate representation of the velocity distribution, may be used to derive estimates of dispersion coefficients. The manner in which data from field tests should be used to derive estimates of dispersion coefficients, however, is a controversial issue. There are both deterministic and stochastic schools of thought, and neither has been conclusively demonstrated in complex hydrogeological settings.

Complicating factors. Certain subtleties of the spatial variability of hydraulic conductivity must be understood because of its key role in the determination of velocity distributions and dispersion coefficients. Hydraulic conductivity is also known as the coefficient of permeability because it is comprised of fluid factors as well as the intrinsic permeability of the stratum in question. This means that a stratum of uniform intrinsic permeability (which depends strictly on the arrangement of its pores) may have a wide range of hydraulic conductivity because of differences in the density and viscosity of fluids that are present. The result is a dramatic downward shift in local flow directions near plumes that have as little as a 1% increase in density relative to uncontaminated water. Such density contrasts frequently occur at landfills and waste impoundments. It is often necessary to correct misimpressions of the direction of a plume because density considerations were not addressed.

Many solvents and oils are highly insoluble in water, and may be released to the subsurface in amounts sufficient to form a separate fluid phase. Because that fluid phase will probably have viscosity and density different from freshwater, it will flow at a rate and, possibly, in a direction different from that of the freshwater with which it is in contact. If an immis-

cible phase has a density approximately the same or less than that of groundwater, this phase will not move down past the capillary fringe of the groundwater. Instead, it will flow along the top of the capillary fringe in the direction of the maximum water-level elevation drop. If the density of an immiscible phase is substantially greater than the groundwater, the immiscible phase will push its way into the groundwater as a relatively coherent blob. The primary direction of its flow will then be down the dip of the first impermeable stratum encountered. There is a great need for better means of characterizing such behavior for site-specific applications. Currently, estimation methods are patterned after multiphase oil reservoir simulators. One of the key extensions needed is the ability to predict the transfer of trace levels of contaminants from the immiscible fluid to the groundwater, such as xylenes from gasoline.

Anisotropy is a subtlety of hydraulic conductivity that relates to structural trends of the rock or sediments of which an aquifer is composed. Permeability and hydraulic conductivity are directionally dependent in anisotropic strata. When molten material from deep underground crystallizes to form granitic or basaltic rocks, for instance, it forms cleavage planes which may later become the preferred directions of permeability. Marine sediments accumulate to form sandstone, limestone, and shale sequences that have much less vertical than horizontal permeability. The seasonal differences in sediments that accumulate on lakebeds, and the stratification of grain sizes deposited by streams as they mature, give rise to similar vertical-to-horizontal anisotropy. Streams also cause anisotropy within the horizontal plane, by forming and reworking their sediments along a principal axis of movement. These structural variations in permeability would be of minimal concern except that water does not flow at right angles to water-level elevation contours under anisotropic conditions. Instead, flow proceeds along oblique angles, with the degree of deviation from a right-angle pathway proportional to the amount of anisotropy. This fact is all too often ignored, and the causes again seem to be a reluctance to conduct the proper field tests, combined with an over-reliance on mathematical modeling.

Table 2—Site characterization—conventional approach.

Actions typically taken
Install a few dozen shallow monitoring wells
Sample and analyze numerous times for 129+ pollutants
Define geology primarily by driller's log and cuttings
Evaluate hydrology with water level maps only
Possibly obtain soil and core samples (chemical extractions)
Benefits
Rapid screening of problem
Moderate costs involved
Field and lab techniques standardized
Data analysis relatively straightforward
Tentative identification of remedial options possible
Shortcomings
True extent of problem often misunderstood
Selected remedial alternative may not be appropriate
Optimization of remedial actions not possible
Clean-up costs unpredictable and excessive
Verification of compliance uncertain and difficult

If the pathways created by cleavage planes and fractures begin to dominate fluid flow through a subsurface stratum, the directions and rates of flow are no longer predictable by the equations used for porous rock and sediments. There have been a number of attempts to represent fractured flow as an equivalent porous medium, but these tend to give poor predictions when major fractures are present and when there are too few fractures to guarantee a minimum degree of interconnectedness. Other representations that have been studied are various dual porosity models, in which the bulk matrix of the rock has one porosity and the fracture system has another. Further development of the dual porosity approach is limited by the difficulty of determining a transfer function to relate the two different porosity schemes. Research in this area needs to be accelerated because there is a great likelihood of fractured flow in just those situations commonly believed to be the most suitable for disposal of hazardous wastes, such as building landfills on "impermeable" bedrock.

Considerations for predictive modeling. Equations for the combined advection-dispersion process are used to estimate the time during which a nonreactive contaminant will travel a specific distance, the pathway it will travel, and its concentration at any point. The accuracy of most predictions is only fair for typical applications because of the complexity of the problems and the scarcity of site-specific hydrogeologic data. The lack of such data can be improved on with much less effort than is commonly presumed, especially when the costs of another round of chemical sampling are compared with the costs of additional borings, core retrievals, geophysical logging, or permeability testing.

Equations that assume a nonreactive contaminant have limited usefulness because most contaminants react with other chemical constituents in subsurface waters and with subsurface solids in a manner that affects the rate at which they travel. Nevertheless, nonreactive advection-dispersion equations are often used to generate "worst-case" scenarios on the presumption that the maximum transport velocity is obtained (equal to that of pure water). This may not be as useful as it first seems. Remedial action

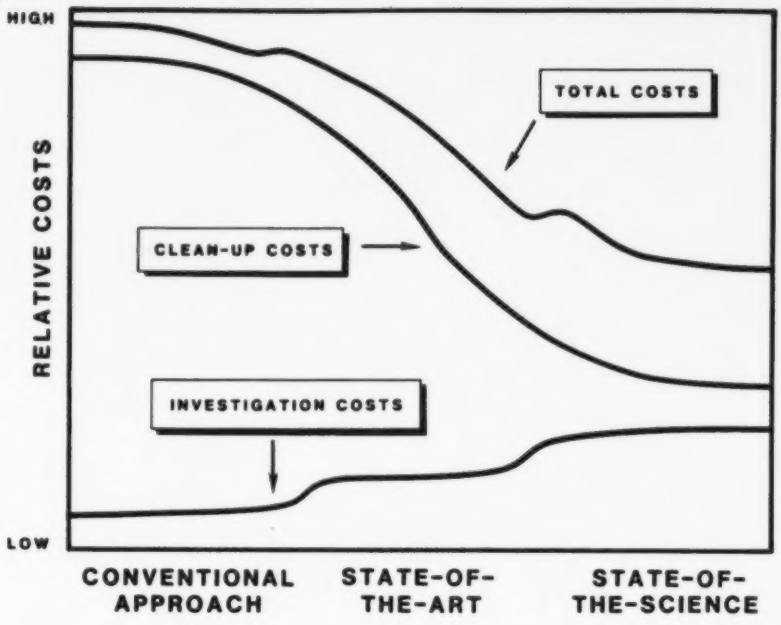

Figure 2—Conceptualization of the trade-offs between investigation and clean-up costs as a function of the sophistication of site characterization efforts.

designs require detailed breakdowns of which contaminants will arrive at extraction wells and when; how long contaminants will continue their slow release from subsurface solids; and whether the contaminants will be transformed into other chemical species by chemical or biological forces. To address these points, special terms must be added to the advection-dispersion equations.

Chemical processes. As difficult as the foregoing complications may be, predicting how chemical contaminants move through the subsurface is a relatively trivial matter when the contaminants behave as ideal, nonreactive substances. Unfortunately, such behavior is limited to a small group of chemicals. The actual situation is that most contaminants will, in a variety of ways, interact with their environment through biological or chemical processes. This section focuses on the dominant chemical processes that may ultimately affect the transport behavior of a contaminant. As with the physical processes previously discussed, some of the knowledge of chemical processes has been translated into practical use in predictive models. However, the science has, in many instances, advanced well beyond what is commonly practiced. Furthermore, there is considerable evidence that suggests numerous undefined processes affect chemical mobility. Most of the deviation from ideal nonreactive behavior of contaminants relates to their ability to change physical form by energetic interactions with other matter. The physical-chemical interactions may be grouped into: alterations in the chemical or electronic configuration of an element or molecule; alterations in nuclear composition; the establishment of new associations with other chemical species; and, interactions with solid surfaces.

Chemical/electronic alterations. The first of these possible changes is typified by oxidation-reduction or redox reactions. This class of reactions is especially important for inorganic compounds and metallic elements because the reactions often result in changes in solubility, complexing capacity, or sorptive behavior, which directly impact on the mobility of the chemical. Redox reactions are reasonably well understood, but there are practical obstacles to applying the known science because it is difficult to determine the redox state of the aquifer zone of interest and to identify and quantify redox-active reactants. Hydrolysis, elimination, and substitution reactions that affect certain contaminants also fit into this classification. The chemistry of many organic contaminants has been well defined in surface water environments. The influence of unique aspects of the subsurface, not the least of which is long residence time, on such transformations of important organic pollutants is currently under investigation. There is also a need to investigate the feasibility of promoting *in situ* abiotic transformations and enhancing the potential for biological mineralization of pollutants.

Nuclear alterations. The second interaction, which results in internal rearrangement of the nuclear structure of an element, is well understood. Radiodecay occurs by a variety of routes, but the rate at which it occurs is always directly proportional to the number of radioactive atoms present. This fact seems to make mathematical representation in contaminant transport models quite straightforward because it allows characterization of the process with a unique, well defined decay constant for each radionuclide.

A mistake that involves the physical form of the reactant is often made when the decay constant is used in models. If the decay constant is applied to the fluid concentrations and no other chemical interactions are allowed, then incorporation of the constant into the subroutine which computes fluid concentrations will not cause errors. If the situation being modeled involves chemical interactions such as precipitation, ion-exchange, or sorption, which temporarily remove the radionuclide from solution, then it is important to use a second sub-

routine to account for the non-solution phase decay of the radionuclide.

Chemical associations. The establishment of new associations with other chemical species is not as well understood. This category includes ion-exchange, complexation, and co-solvation. The lack of understanding derives from the non-specific nature of these interactions, which are, in many instances, not characterized by the definite proportion of reactants to products (stoichiometry) typical of redox reactions. While the general principles and driving mechanisms by which these interactions occur are known, the complex subsurface matrix in which they occur provides many possible outcomes and renders predictions uncertain.

Ion-exchange and complexation reactions heavily influence the mobility of metals and other ionic species in the subsurface in a reasonably predictable fashion. Their influence on organic contaminant transport, however, is not well understood. Based on studies of pesticides and other complex organic molecules, natural organic matter (such as humic and fulvic materials) can complex and thereby enhance the apparent solubility and mobility of synthetic organic chemicals. Research is needed to define the magnitude of such interactions, not only with naturally occurring organic molecules but also with man-made organics in contaminated environments. Research is also needed to determine if these complexes are stable and liable to transport through the subsurface. Examination of the degree to which synthetic organic chemicals complex toxic metals is also necessary. There is no theoretical objection to such interactions, and there is ample evidence that metals are moving through the subsurface at many waste sites.

Co-solvation occurs when another solvent is in the aqueous phase at concentrations that enhance the solubility of a given contaminant. This occurs in agricultural uses, for example where highly insoluble pesticides and herbicides are mixed with organic solvents to increase their solubility in water prior to field application. There is every reason to expect similar behavior at hazardous waste sites, where a variety of solvents are typically available. At present, prediction of the extent of the solubility increases that might occur at disposal sites in the complex mixture of water and organic solvents is essentially impossible. Researchers have started examining co-solvation as an influence on pollutant transport, by working on relatively simple mixed solvent systems. This research will be extremely useful, even if the results are limited to a qualitative appreciation for the magnitude of the effects.

At the extreme, organic solvents in the subsurface may result in a phase separate from the aqueous phase. In addition to movement of this separate phase through the subsurface, contaminant mobility that involves partitioning of organic contaminants between the organic and aqueous phases must also be considered. The contaminants will move with the organic phase and will, depending on aqueous phase concentrations, be released into the aqueous phase to a degree roughly proportional to their octanol-water partition coefficients. An entire range of effects is possible, from increasing to slowing the mobility of

Table 3—Site characterization—state-of-the-art approach.

Recommended actions
Install depth-specific well clusters
Sample and analyze for 129+ pollutants initially
Analyze selected contaminants in subsequent samplings
Define geology by extensive coring/split-spoon samples
Evaluate hydrology with well clusters and geohydraulic tests
Perform limited tests on solids (grain size, clay content)
Conduct limited geophysical surveys (resistivity soundings)
Benefits
Conceptual understanding of problem more complete
Better prospect for optimization of remedial actions
Predictability of remediation effectiveness increased
Clean-up costs lowered, estimates improved
Verification of compliance more soundly based
Shortcomings
Characterization costs somewhat higher
Detailed understanding of problem still difficult
Full optimization of remedial actions not likely
Field tests may create secondary problems
Demand for specialists increased

Table 4—Site characterization—state-of-the-science approach.

Idealized approach
Assume state-of-the-art approach as starting point
Conduct tracer-tests and borehole geophysical surveys
Determine percent organic carbon, exchange capacity, and other properties of solids
Measure redox potential, pH, dissolved oxygen, and other properties of fluids
Evaluate sorption-desorption behavior using select cores
Identify bacteria and assess potential for biotransformation
Benefits
Thorough conceptual understanding of problem obtained
Full optimization of remedial actions possible
Predictability of remediation effectiveness maximized
Clean-up costs lowered significantly, estimates reliable
Verification of compliance assured
Shortcomings
Characterization costs significantly higher
Few previous field applications of advanced theories
Field and laboratory techniques not yet standardized
Availability of specialized equipment low
Demand for specialists dramatically increased

the chemical in the subsurface relative to its migration rate in the absence of the organic phase. The equilibrium partitioning process increases the total volume of groundwater affected by contaminants, by releasing a portion of the organic phase constituents into adjacent waters. It may also interfere with transformation processes by affecting pollutant availability for reaction, or by acting as a biocidal agent to the native microflora.

Surface interactions. Of those interactions that involve organic chemicals in the environment, none has been as exhaustively studied as sorption. Sorption studies relate, in terms of a sorption isotherm, the amount of contaminant in solution to the amount associated with the solids. The contaminant is partitioned between the solids and the aqueous phase at ratios independent of (linear isotherms) or dependent on (non-linear isotherms) the equilibrium solution concentration. Sorption isotherms for nonpolar organic compounds commonly diverge from linearity well before the contaminant aqueous solubility becomes a consideration. Linear or non-linear partition coefficients derived from sorption isotherms can be used to approximate contaminant retardation in the subsurface.

Most often the sorption term in transport models is estimated for simplicity from the assumption that the response is linear. This approximation can produce serious mass balance errors. Typically, the contaminant mass in the solution phase is underestimated and contaminant retardation is thereby overestimated. In practical applications this means that the contaminant can be detected at a monitoring well long before it is anticipated. To resolve the discrepancy between predicted and actual transport, most practitioners arbitrarily adjust some other poorly characterized model parameter (for example, dispersion). This leads to creation of a model that does not present various natural process influences in proper perspective. The predictions from such models are likely to be qualitatively, as well as quantitatively incorrect. More widespread consideration should be given to accurate representation of non-linear sorption, particularly in transport modeling at contaminated sites.

The time dependency of the sorption process is a related phenomenon that has also been largely ignored in practical applications of sorption theory. Most models assume that sorption is instantaneous and completely reversible. A growing body of evidence argues to the contrary, not only for large organic molecules in high-carbon soils and sediments, but also for solvent molecules in low-carbon aquifer materials. Sorption and desorption kinetics are undoubtedly important in contaminant transport, but the implications have yet to be systematically defined. In fairly homogenous aquifers, retardation of relatively mobile contaminants in the field can be reasonably predicted from batch studies. Sorption kinetics may cause deviations from batch observations in more complex systems, especially when contaminant concentrations force sorption isotherms into a non-linear response. Additionally, there must be some subtle interplay between sorption kinetics and groundwater flow rates which gains significance in pump-and-treat remediation efforts where flow rates are routinely substantially increased.

Evidence from Superfund sites and ongoing research activities suggests that contaminant association with a surface does not preclude mobility. In many instances, especially in glacial tills that contain a wide distribution of particle sizes, fine aquifer materials have accumulated in the bottom of monitoring wells. Iron-based colloids have been identified in groundwaters downgradient from a site contaminated with domestic wastewater. If contaminants can associate with these fine particles, their mobility through the subsurface could be markedly enhanced. To determine the significance of particle transport to pollutant movement, studies must be performed at such contaminated sites.

Although knowledge about chemical processes that function in the subsurface has been significantly expanded in recent years, this information is only slowly finding its way into practical interpretations of pollutant transport at contaminated sites. Evidence from field sites suggests that much remains to be learned about these processes.

Biological processes. Many contaminants that enter the subsurface environment are biologically reactive. Under appropriate circumstances they can be completely degraded to harmless products. Under other circumstances, however, they can be transformed to new substances that are more mobile or more toxic than the original contaminant. Quantitative predictions of the fate of biologically reactive substances are at present very primitive, particularly compared to other processes that affect pollutant transport and fate. This situation resulted from the scientific equivalent of mixed metaphors. The groundwater community chose an inappropriate paradigm around which to weave their equations and computer codes. Only very recently has detailed field work revealed the inadequacy of the prevailing view. With this artificial impediment removed, rapid progress in predicting biological transformations can be expected.

The surface water model. As little as 5 years ago groundwater scientists considered aquifers and soils below the zone of plant roots to be essentially devoid of organisms capable of transforming contaminants. As a result, there was no reason to include terms for biotransformations in transport models. Recent surveys have shown that water-table aquifers harbor appreciable numbers of metabolically active microorganisms, and that

these microorganisms frequently can degrade organic contaminants. It became necessary to at least consider biotransformation in the transport models. Unfortunately many groundwater scientists adopted the conceptual model most frequently used to describe biotransformations in surface waters. The presence of the contaminant was assumed to have no effect on microorganism populations that degrade it. It was also assumed that contaminant concentration does not influence transformation kinetics, and that the capacity to transform the contaminant is uniformly distributed throughout the body of water under study. These assumptions are often appropriate for surface waters: contaminant concentration is usually too low and the residence time too short to allow adaptation of the microbial community to the contaminant, and the organisms that are naturally pre-adapted to the contaminant are mixed throughout the water body by turbulence. As a result, utilization kinetics can conveniently be described by simple first-order decay constants. In surface water these constants are usually obtained by monitoring contaminant disappearance in water samples.

Groundwater biotransformations. These circumstances rarely apply to biotransformation in groundwaters. Contaminant residence time is usually long, at least weeks or months, and frequently years or decades. Further, contaminant concentrations that are high enough to be of environmental concern are often high enough to elicit adaptation of the microbial community. For example, the U.S. Environmental Protection Agency maximum contaminant level (MCL) for benzene is 5 μg/L. This is very close to the concentration of alkylbenzenes required to elicit adaptation to this class of organic compounds in soils. As a result, the biotransformation rate of a contaminant in the subsurface environment is not a constant, but increases after exposure to the contaminant in an unpredictable way. Careful field work has shown that the transformation rate in aquifers of typical organic contaminants, such as alkylbenzenes, can vary as much as two orders of magnitude over a metre vertically and a few metres horizontally. This surprising variability in transformation rate is not related in any simple way to system geology or hydrology.

It is difficult to determine first-order rate constants in subsurface material. Most microbes in subsurface material are firmly attached to solid surfaces; usually less than 1% of the total population is truly planktonic. As a result, the microbes in a groundwater sample grossly underrepresent the total microbial population in the aquifer. Thus, contaminant disappearance kinetics in a groundwater sample do not represent the behavior of the material in the aquifer. It is therefore necessary to do microcosm studies with samples representative of the entire aquifer system—a formidable technical challenge.

A groundwater model. These concerns have prompted re-examination of assumptions about biotransformation implicit or explicit in a particular modeling approach, with the realization that no one qualitative description of biotransformation can be universally applicable. Field experience has shown that the laws that govern the biological fate of contaminants actually change within aquifers in response to geochemical constraints on microbial physiology. Rather than describing biotransformation with a continuous function applicable to all points in the aquifer, it may be more realistic to examine key geochemical parameters and to use that information to identify the relationship for biotransformation that applies at any particular point. These key parameters could include contaminant concentration, oxygen or other electron acceptor concentration, redox state, pH, toxicity of the contaminant or co-occurring materials, and temperature. One such model has been evaluated in the field.

The model described an alkylbenzene and polynuclear aromatic hydrocarbon plume in a shallow water-table aquifer. Microcosm studies showed that organisms in the aquifer had adapted to these contaminants, and would degrade them very rapidly when oxygen was available. As a result of this adaptation, the hydrocarbon biodegradation rate was not controlled by any inherent property of the organisms. Rather, physical transport processes such as diffusion and dispersion seemed to dominate by controlling oxygen availability to the plume. Because the biotransformation rate was controlled by physical processes, the actual model was very simple. Oxygen and hydrocarbon transport were simulated as conservative solutes using U.S. Geological Survey method-of-characteristics code. A subroutine examined the oxygen and hydrocarbon concentrations at each node and generated new concentrations based on oxidative metabolism stoichiometry. When the model was projected forward in time it illustrated an important property of many such plumes. The plume grew with time until the rate of admixture of oxygen balanced the rate of release of hydrocarbons from the source. Afterward, the extent of the plume was at steady state.

The body of field experience which can be drawn on to properly assign laws for biotransformation is growing rapidly. Transport-limited kinetics may commonly apply to releases of petroleum hydrocarbons and other easily degradable materials such as ethanol or acetone in oxygenated groundwaters. On the other hand, materials that can support a fermentation, in which an exogenous electron acceptor is not required, may follow first-order kinetics. Unfortunately, many important biotransformations in groundwater are still mysteries. The reductive dehalogenation of small halogenated hydrocarbons such as tri-

chloroethene and 1,1,1-trichloroethane is a good example. In such cases transformation kinetics of the compound are controlled by the transformation kinetics of a second compound, the primary substrate that supports the metabolism of the active microorganisms. These complex interactions are poorly understood and cannot be described quantitatively at the present time. However, this is an area of active research, and the appropriate relationships may soon be determined.

It is time to put these new perspectives to work. Rapid field methods to determine if adaptation has occurred at a site are needed. Tools to predict whether adaptation can be expected, and to estimate the time required for adaptation if it does occur are also necessary. For systems that are limited by transport processes, field methods to estimate the aquifer processes that control mixing, such as transverse dispersion and exchange processes across the water table are required. For systems that are limited by the intrinsic biotransformation rate, new laboratory test methods, possibly improved microcosms, that will provide reliable estimates of the kinetic parameters are required. In addition to being sufficiently accurate and precise, these new methods should provide estimates that are truly representative of the hydrologic unit being simulated. Because contaminants typically have long residence times in aquifers, slow transformation rates can have environmental significance. The test methods should also be sufficiently sensitive to measure transformation rates that are significant in the hydrologic context being simulated. Finally, there is a need for models that go beyond a simple prediction of the contaminant concentration at some point in the aquifer and forecast the concentrations produced by production wells.

Summary

The evolution of concepts pertinent to investigating and predicting the movement of contaminants in the subsurface has been described. This was done for two reasons. There seems to be widespread overconfidence among those not directly involved in groundwater quality research regarding the ability to predict transport and fate of contaminants in the subsurface. The preceding discussion should place in proper perspective the admittedly remarkable advances that have been made in recent years, by illustrating the practical implications of conceptual uncertainties that remain unresolved. There is also far too little emphasis on obtaining detailed information about the potential pathways and mechanisms that affect transport at any given site.

Additional effort devoted to site-specific characterizations of natural process parameters, rather than relying almost exclusively on chemical analyses of groundwater samples, can significantly improve the quality and cost-effectiveness of the remedial actions at such sites. To underscore this point, condensed summaries are provided of the principal activities, benefits, and shortcomings of three possible site characterization approaches: conventional (Table 2), state of the art (Table 3), and state of the science (Table 4). To further illustrate this, a qualitative assessment of desired tradeoffs between characterization and clean-up costs is presented in Figure 2. As illustrated there, some investments in specialized equipment and personnel will be needed to make the transition to more sophisticated approaches, but those investments will be more than paid back in reduced clean-up costs. The maximum return on increased investments is expected for the state-of-the-art approach, and will diminish as the state-of-the-science approach is reached because highly specialized equipment and personnel are not widely available. It is vitally important that this philosophy be considered because the probable benefits in lowered total costs, health risks, and time can be substantial.

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